

Chapter 7

ADSORPTION ISOTHERMS

Abstract A short overview of adsorption isotherms often used (i) to correlate adsorption equilibria data for sorbent materials characterization and (ii) for design of industrial gas adsorption processes is given. The basic types of adsorption isotherms observed experimentally are discussed in brief. The Langmuir adsorption isotherm (LAI) and certain of its extensions to (energetically) heterogeneous sorbent materials and to admolecules with interactions are presented (Sect. 2). Several empirical isotherms used for micro- and mesoporous materials showing pore condensation are discussed in Sect. 3 briefly. In Sect. 4 an outline of thermodynamics of adsorbate phases of fractal dimension is given. Several isotherms are presented which are generalizations of well-known isotherms (Langmuir, BET, etc.) to multicomponent adsorbates on heterogeneous surfaces. These isotherms are solutions of Maxwell's relations of the underlying Gibbs fundamental equation of the adsorbed phase. List of symbols. References.

1. INTRODUCTION

The purpose of this chapter is to give a comprehensible overview of a few frequently used adsorption isotherms (AIs) for single- and multicomponent gas adsorption systems. The adsorption isotherm (AI) is, in the sense of thermodynamics, the thermal equation of state [7.81] for the adsorbed phase, i. e. a function

$$m = m(p, T, m^s)$$

for single component systems, or a set of functions

$$m_i = m_i(p_1 \dots p_N, T, m^s), \quad i = 1 \dots N,$$

for a multicomponent system. Here (m) and $(m_1 \dots m_N)$ indicate the mass(es) of components ($i = 1 \dots N$) adsorbed, $p_i = y_i p$ is the partial pressure of compo-

ment i in the gas phase with molar concentration (y_i) and T is the temperature of the system. The parameter (m^s) indicates the mass of the sorbent material.

As many isotherms, especially for single component systems, already have been developed during a period of nearly 100 years, it is not possible within this monography to present all of them. Instead we will restrict the discussion to those which proved to be useful for engineering applications or at least have the potential to be so, especially in higher pressure regimes ($p \simeq 10 \text{ MPa}$) and in a broad temperature interval ($200 \text{ K} < T < 400 \text{ K}$). Good overviews of adsorption isotherms can be found in [7.1-7.4]. Hints to additional literature will be given whenever it is appropriate.

Adsorption isotherms (AI) are used for (i) characterization of porous solids and (ii) design of industrial adsorption processes. Here they are needed not only for single- but also for multicomponent gas mixture systems. Due to the complexity of interactions of admolecules (a) with the atoms and molecules of the sorbent material (s) (a - s -interactions) [7.5-7.7], it is not possible today to calculate AIs either “*ab initio*” by statistical molecular methods (DFT or other methods from Statistical Mechanics) or by phenomenological methods based on a few macroscopic or microscopic data of the sorptive-sorbent system. Even ideal molecular models of surfaces and pores of sorbent materials need not only model functions for the (a - s)-interactions, but in principle will lead to a so-called calibration problem [7.8] which only can be solved by introducing experimental data regarding absolute amounts or masses of gas adsorbed at well defined conditions [7.9]. As these are fairly cumbersome to measure and normally are not available at all, cp. remarks in Chap. 1, it is necessary to measure gas adsorption equilibria data, especially for multicomponent systems, i. e. so-called coadsorption equilibria data. These often exhibit or at least indicate the physical mechanism of the adsorption process observed and thus allow one to make a proper choice for an analytical AI to correlate the data and then to try to extrapolate them to other pressures and temperatures needed for process design. As in most industrial sorbent materials both micro- and mesopores occur to a more or lesser extent, one often can find a combination of basically different adsorption mechanisms like surface coverage and pore condensation to occur, thus leading to fairly complex AIs the structure of which cannot be foreseen without any experimental information.

Adsorption equilibria data normally are graphically presented as

- Isotherms : m, p -diagrams at $T = \text{const.}$,
- Isobars : m, T -diagrams at $p = \text{const.}$,
- Isosteres : $\ln(p/p_0), T$ -diagrams at $m = \text{const.}$

Typical examples for these curves often observed for microporous materials are sketched in Table 7.1. In addition adsorption enthalpies are often needed for process design. In view of space limitations we do not consider them here but refer to the literature [7.2, 7.5, 7.10, 7.11].

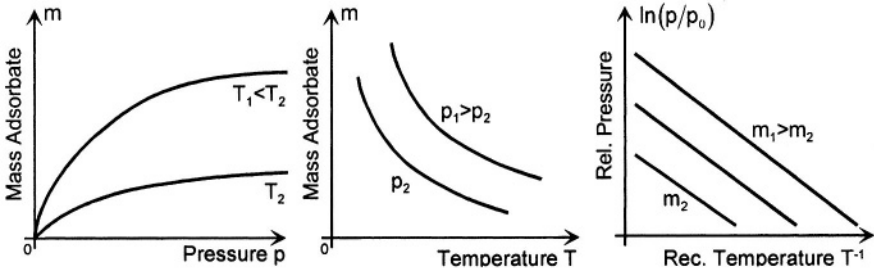


Table 7.1. Representation of gas adsorption equilibria data as isotherms ($T = \text{const}$), isobars ($p = \text{const}$), and isosteres ($m = \text{const}$).

The experimentally observed adsorption isotherms (AI) can be classified according to IUPAC-recommendations in 6 different types I-VI [7.1-7.3, 7.5, 7.12, 7.13]. Recently some subclasses of these have been introduced [7.5], but are not considered here. A scheme of these types of AIs is given in Tab. 7.2, [7.2, 7.5, p 19].

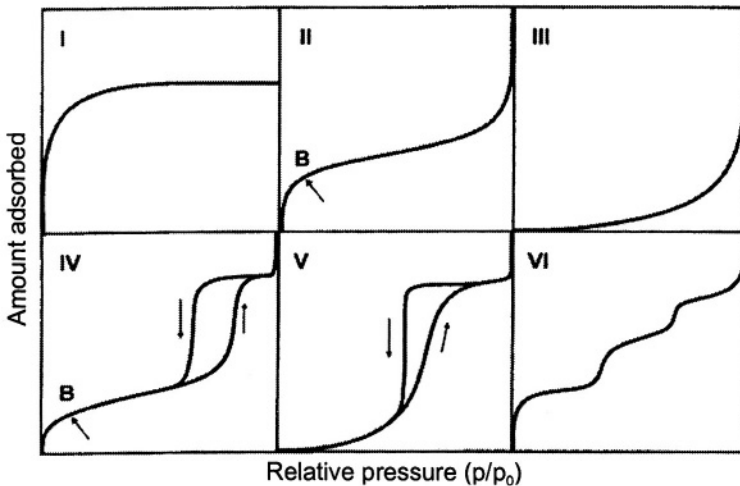


Table 7.2. Main types of gas physisorption isotherms (IUPAC, 1985).

Type I isotherms can be described by the Langmuir equation, cp. Sect. 2.1. They are characterized by a horizontal plateau, i. e. the asymptotic value the mass adsorbed approaches and maintains for even very high gas pressures.

These isotherms are characteristic for microporous materials showing micropore filling but no multilayer adsorption.

Example: Water on zeolite or inorganic (i. e. polar) molecular sieves. Organic vapors (C_nH_{2n+2}) on zeolites and molecular sieves.

Remarks: 1. Chemisorption systems often also show AIs of Type I.
2. The BET method cannot be applied to measure the surface area of the microporous materials, cp. [7.14].

Type II isotherms describe typically adsorption in mesoporous materials showing at low pressures monolayer, at higher pressures near saturation multilayer adsorption and pore condensation but no hysteresis. These isotherms also can be observed in disperse, nonporous or only macroporous solids. (pore diameter > 50 nm). They often can be described by the BET equation or its generalizations, cp. Sects. 3.4, 4.2.

Example: Vapors of polar media (H_2O , CCl_4 , F_kH_{4+i-k}) on molecular sieves, vapors of non-polar organic substances on slightly microporous but mainly mesoporous activated carbons.

Type III isotherms occur in systems where the adsorbate-sorbent (a-s) interaction is small compared to the adsorbate-adsorbate (a-a) interaction, i. e. strongly associating admolecules.

Example: Water on activated carbon and hydrophobic zeolites (DAY, Degussa).

Type IV isotherms describe the adsorption behavior of special mesoporous materials showing pore condensation together with hysteresis behavior between the adsorption and the desorption branch.

Example: Water vapor from humid air on special types of activated carbons and hydrophilic zeolites.

Type V isotherms deviate from Type IV curves by nearly perpendicular middle portions of the adsorption and the desorption branches often near relative gas pressures $p/p_s(T) \cong 0.5$, indicating the existence of mesopores in which phase change like pore condensation may occur.

Example: Water on special activated carbons and carbon molecular sieves.

Type VI isotherms present stepwise multilayer adsorbates, the layers becoming more pronounced at low temperatures.

Example: Nonpolar, spherical molecules (noble gases) on planar graphite surfaces, butanol (C_4H_9OH) on aluminum silicate.

A much more detailed analysis of these isotherms and their molecular interpretation is given in [7.1, 7.3, 7.5], cp. also [7.62].

In this chapter we are going to discuss the Langmuir adsorption isotherm (LAI) and several of its generalizations for single- and multicomponent systems in Sect. 2. This isotherm has proved to be most useful to describe adsorption in microporous materials. In Sect. 3 we will provide some information on a few empirical adsorption isotherms used to describe gas adsorption in micro- and mesoporous materials, i. e. showing pore condensation leading to an unlimited amount of mass in the adsorbed phase.

In Sect. 4 we present several adsorption isotherms which are solutions of the Maxwell relations of the Gibbs fundamental equation of the multicomponent adsorbate [7.15]. These isotherms are thermodynamically consistent generalizations of several of the empirical isotherms presented in Sect. 3 to (energetically) heterogeneous sorbent materials with surfaces of fractal dimension. In Sect. 5 some general recommendations for use of AIs in industrial adsorption processes are given.

2. SIMPLE MOLECULAR ISOTHERMS

2.1 Langmuir Adsorption Isotherm

The classical Langmuir adsorption isotherm and several of its generalizations are presented. The physical background is enlightened and hints for engineering applications are given. The generalizations refer to

- a) real gas adsorptives,
- b) energetically heterogeneous sorbent materials,
- c) admolecules with interactions.

For more information the reader is referred to the vast and still growing literature of adsorption, experiments, theory, numerical simulation and engineering applications [7.1-7.5].

2.1.1 Classical Form

The classical form of the Langmuir adsorption isotherm (LAI) already published in 1916, [7.16] is

$$m(p, T, m^s) = m_\infty(T, m^s) \frac{b(T)p}{1 + b(T)p} \tag{7.1}$$

Parameters:

- $m = Mn$ Mass of adsorbate
- p pressure
- T Absolute temperature
- m^s mass of sorbent material
- $m_\infty = \lim_{p \rightarrow \infty} m$ limiting value of mass adsorbed at $T = \text{const}$, $p \rightarrow \infty$.
Also mass of a monolayer adsorbate covering completely the surface of the sorbent [7.3].

$$m_\infty(T, m^s) = \mu_\infty(T_0) \left(\frac{T_0}{T} \right)^{k_s} m^s, \quad k_s > 0 \tag{7.2}$$

μ_∞ limiting mass ($p \rightarrow \infty$) of adsorbate on sorbent of mass (m^s) at reference temperature (T_0).

$$b(T) = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} \exp\left(\frac{q}{RT}\right) \dots \text{Langmuir parameter}$$

also reciprocal of half-loading pressure, cp. (7.1), [7.3, 7.76]

$$b^{-1} = p(T, m = m_\infty/2, m^s), \tag{7.3}$$

$R=R/M$ specific gas constant.

Enthalpy of adsorption

$$\Delta H = H^a - H^f = -qm < 0 \tag{7.4}$$

$q = \text{const}$ specific heat of adsorption assumed to be constant [7.5, 7.33]

Enthalpy of desorption:

$$H^f - H^a = -\Delta H = qm > 0. \tag{7.4a}$$

Physical prerequisites of the LAI (7.1); cp. also Fig. 7.1.

1. Adsorption occurs on a fixed number of sites.
2. Each site can only take one admolecule but no more.
3. All sites are energetically equivalent ($q = \text{const}$), cp. (7.4)
4. Interactions between adsorbed molecules are neglected as they are assumed to be small compared to the sorbate / sorbent interactions characterized by the (specific) adsorption energy (q) [7.18, 7.64].

The energetic situation of the admolecules in a Langmuir adsorbate is sketched in Figure 7.1. A graphic representation of the LAI, Eq. (7.1) is given in Fig. 7.2

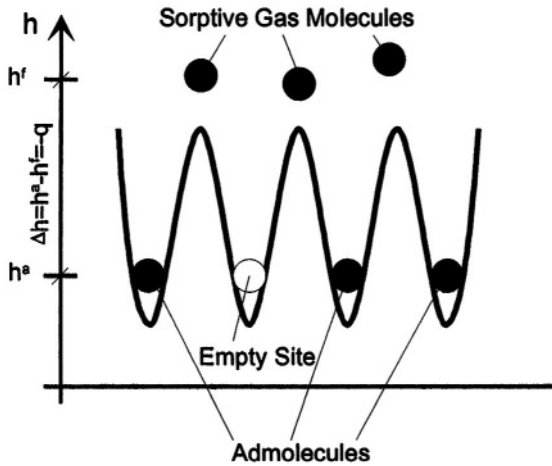


Figure 7.1. Energetic scheme of a Langmuir adsorbate. All adsorption sites can only take one molecule. All admolecules are isolated from each other so that no interactions between them have to be taken into account.

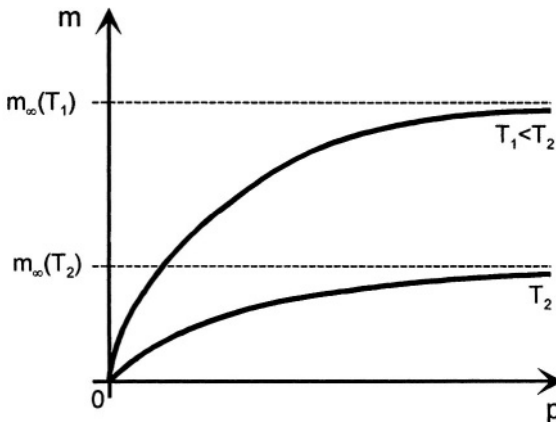


Figure 7.2. The classical Langmuir adsorption isotherm (LAI) sketched for two different temperatures ($T_1 < T_2$). The limiting loadings increase with decreasing temperature, i. e. $m_\infty(T_2) < m_\infty(T_1)$.

The classical LAI (7.1) seems to be the limiting form of all gas adsorption isotherms for high temperatures. This simply can be explained by the fact that for $T \rightarrow \infty$ the average (specific) thermal energy (RT) of the ideal sorptive gas is much larger than the adsorption energy (q), i. e. $RT \gg q$. Under such conditions the sorbent surface appears to be nearly homogeneous for all admolecules. Also the interaction energy of admolecules represented by the heat of evaporation / condensation ($r < q$) can be neglected. Hence the prerequisites for the LAI given above hold and Langmuirian behavior of the AI should be expected.

The LAI (7.1) easily can be converted to calculate the gas pressure (p) needed to maintain a certain amount of mass (m) adsorbed on (m^s):

$$p(m, T, m^s) = \frac{1}{b(T)} \cdot \frac{m}{m_\infty(T, m^s) - m} \quad 7.5$$

A graphical representation of this function can easily be deduced from Fig. 7.1 by interchanging the coordinate axes ($p \leftrightarrow m$).

To represent experimental data and check graphically their consistency, a linearized in (p) version of (7.1) is often useful. It reads

$$\frac{p}{m} = \frac{1}{bm_\infty} + \frac{p}{m_\infty} \quad 7.6$$

Scattering of data around this straight line in a (p/m , p)-diagram often indicates experimental inconsistencies, especially at low pressures ($p \rightarrow 0$, $m \rightarrow 0$).

The isosteres of the LAI, i. e. curves $p = p(T, m = \text{const}, m^s)$ easily can be calculated from eqs. (7.1, 7.2) as

$$\ln \left(\frac{p}{p_0} \sqrt{\frac{T_0}{T}} \right) = -\frac{q}{RT_0} \left(\frac{T_0}{T} \right) + \ln \left(\frac{m/m_\infty}{1 - (m/m_\infty)} \right) \quad 7.7$$

Here (T_0) is a reference temperature which can be chosen arbitrarily.

A graphical representation of this function is given in Figure 7.3.

At higher pressures it may be necessary to take real gas effects of the sorptive medium into account. A simple way to do this is, to replace the

pressure (p) in Eq. (7.1) by the fugacity $f = f(T, P)$ of the gas [7.17]. We then get

$$m(p, T, m^s) = m_\infty(T, m^s) \frac{b(r)f(p, T)}{1 + b(r)f(p, T)} \tag{7.8}$$

Adsorption isotherms of this type have proved to be useful to describe adsorption of small molecule gases like ($\text{CH}_4, \text{N}_2, \text{O}_2$) at ambient temperature and pressures up to 50 MPa, [7.80]. The enthalpy of adsorption then is, cp. Eq. (7.4):

$$\Delta H = H^a - H^f = - \left(q - \frac{RT^2}{f} \left(\frac{\partial f}{\partial T} \right)_p \right) m \tag{7.8a}$$

We finally want to draw reader’s attention to the energetic situation of the classical Langmuir adsorbate described by Eq. (7.1).

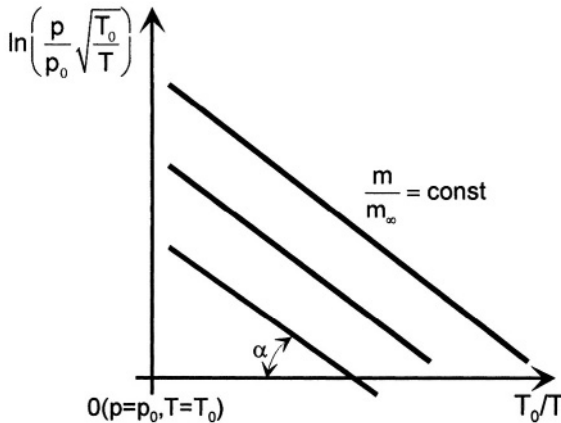


Figure 7.3. Isosteres $p = p(T, m = \text{const}, m^s)$ of the classical Langmuir adsorption isotherm, Eq. (7.7).

It is characterized by a single constant (q) which is – according to (7.4) – the specific change, i. e. increase of the enthalpy of the sorptive gas due to desorption for an adsorbate mass $0 \leq m \leq m_\infty$.

$$\Delta h_{\text{des}} = \frac{\Delta H}{m} = +q > 0 \tag{7.9}$$

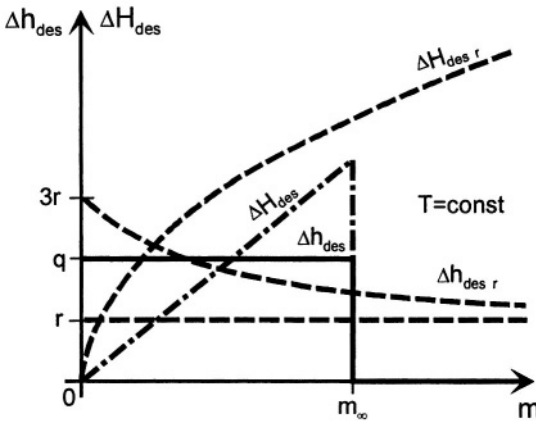


Figure 7.4. Specific enthalpy of desorption of a Langmuir adsorbate (Δh_{des}) and a real adsorbate ($\Delta h_{des,r}$). The integral enthalpies of desorption ($\Delta H_{des}, \Delta H_{des,r}$) also have been sketched qualitatively.

In Figure 7.4 this curve is sketched together with the differential heat of desorption of a real, i. e. energetically heterogeneous adsorbed phase

$$\Delta h_{des,r} = \left(\partial(H^h - H_r^a) / \partial m \right)_T \tag{7.9a}$$

Here (H_r^a) is indicating the enthalpy of the real adsorbed phase of mass (m).

The curve $\Delta h_{des,r}(m)$ in Fig. 7.4 starts for $m = 0$ at values which are about three times the heat of evaporation (r) of the liquid sorptive medium at the temperature (T) considered. (For $T > T_c$ use the Riedel-line approximation, cp. Eq. (7.23) and [7.17]). This curve approaches for $m \rightarrow \infty$ the heat of evaporation (r) asymptotically. A comparison of the curves $\Delta h_{des}(m)$ and $\Delta h_{des,r}(m)$ in Figure 7.4 clearly shows the limitations of the Langmuir adsorption model leading to the isotherm (7.1), but also its main advantage, namely its simplicity.

Langmuir originally based the derivation of the adsorption isotherm (7.1) on kinetic arguments which for sake of completeness are mentioned here in brief [7.2 – 7.4, 7.7, 7.15, 7.19, 7.20]:

1. The number of molecules (dn^+) which are adsorbed on a surface including a fixed maximum number ($n_\infty = m_\infty/M$) of adsorption sites within the

differential time interval (dt) is proportional to the number of empty sites ($n_\infty - n$) and the pressure (p) of the adsorptive

$$dn^+ = k^+ p (n_\infty - n) dt, \quad 7.10$$

k^+ being a positive constant.

2. The number of molecules (dn^-) which desorb from the surface within (dt) is proportional to the number (n) of molecules already adsorbed:

$$dn^- = k^- n dt, \quad 7.11$$

k^- being a positive constant.

Hence we have for the net gain of molecules adsorbed within (dt)

$$dn = dn^+ - dn^- \quad 7.12$$

from (7.10, 7.11).

$$\frac{dn}{dt} = k^+ p n_\infty - (k^+ p + k^-) n \quad 7.13$$

This ordinary differential equation (ODE) has the solution

$$n(t) = n_0 e^{-at} + n_\infty \frac{bp}{1 + bp} (1 - e^{-at}) \quad 7.14$$

with

$$a = k^+ p + k^-, \quad b = \frac{k^+}{k^-} \quad 7.15$$

and $n_0 = n(0)$, cp. Fig. 7.5. For $t \rightarrow \infty$ or, likewise $(dn/dt) = 0$, we get either from (7.13) or (7.14) after multiplication with the mole mass (M) of the sorptive gas the equilibrium value of the sorbate mass

$$m_{\text{eq}} = m_\infty \frac{bp}{1 + bp}$$

which is the LAI, Eq. (7.1).

For more information on the kinetics of adsorption processes the reader is referred to the literature, especially to the review articles by W. Rudzinski and Panczyk [7.19], [7.20] and the monograph by D. D. Do [7.3].

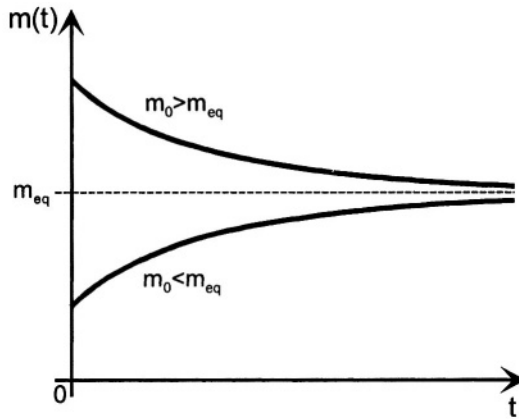


Figure 7.5. Kinetics of a Langmuir adsorption process with initial adsorbate mass $m_0 = n_0M$ and asymptotic mass $m(\infty) = m_\infty = n_\infty M$. The time of relaxation of the process is given by $\tau = 1/a_0 \cdot 1/(k^+p + k^-)$.

The Langmuir model of adsorption easily can be extended to multi-component adsorption processes [7.2 Chap. 4.6, 7.3 Chap. 5, 7.29, 7.75, 7.76]. The resulting adsorption isotherm is

$$m_i(p_1 \dots p_N, T, m^s) = m_{i\infty}(T, m^s) \frac{b_i p_i}{1 + \sum_{k=1}^N b_k p_k}, \quad i = 1 \dots N \quad 7.16$$

Parameters:

- $m_i = n_i M_i$... mass of component $i = 1 \dots N$ of the adsorbed phase
- $p_i = y_i p$... partial pressure of component (i) with molar fraction (y_i) in the sorptive gas mixture at pressure (p).
- $m_{i\infty} = \lim_{\substack{p_i \rightarrow \infty \\ p_k = 0}} m_i$... limiting value of pure component (i) adsorbed at $T = \text{const}$ for $p_i = p \rightarrow \infty$. Also mass of a monolayer of component (i) covering completely the surface of the sorbent material.

$$b_i(T) = \frac{1}{p_{0i}} \sqrt{\frac{T_{0i}}{T}} \exp\left(\frac{q_i}{R_i T}\right), \quad i = 1 \dots N \quad 7.17$$

Langmuir parameter, also reciprocal of half-loading partial pressure, cp. (7.16):

$$\begin{aligned} b_i^{-1}(T) &= p_i(T, m_i = m_{i\infty} / 2, m^s), \quad 1 \dots N. \\ R_i &= R/M_i \dots \text{specific gas constant} \\ q_i &\dots \text{specific enthalpy of desorption of pure component (i)}. \end{aligned}$$

The adsorption isotherms (7.16) easily can be converted to give the partial gas pressures ($p_1 \dots p_N$) necessary for maintaining a given set of masses ($m_1 \dots m_N$) in the adsorbed state:

$$p_i(m_1 \dots m_N, T, m^s) = \frac{1}{b_i(T)} \cdot \frac{m_{i\infty}(T, m^s)}{1 - \sum_{k=1}^N (m_k / m_k(T, m^s))}, \quad i = 1 \dots N \quad 7.18$$

For small pressure values ($p_i \rightarrow 0, i = 1 \dots N$) the isotherms (7.16) can be linearized. Then we have for the mole numbers of the adsorbed components

$$n_i = n_{i\infty} b_i p_i + O(p_i^2) \quad 7.19$$

with the Henry constants defined by

$$H_i = n_{i\infty} b_i, \quad i = 1 \dots N \quad 7.20$$

Hence we get for the so-called separation factors of components (i, k) in the gaseous and the adsorbed phase defined by

$$\begin{aligned} S_{ik} &= (x_i / y_i) / (x_k / y_k), \quad i, k = 1 \dots N \\ &= \frac{n_i p_k}{n_k p_i} \end{aligned} \quad 7.21$$

in view of (7.19, 7.20)

$$S_{ik} = \frac{H_i}{H_k}, \quad i, k = 1 \dots N \quad 7.22$$

The symbols on the r.h.s of (7.21) indicate respectively the molar concentrations of components (i, k) in the adsorbate (x_i, x_k) and the sorptive phase (y_i, y_k). The practical value of cp. (7.22) is that low pressure

measurements of the binary coadsorption equilibria, which deliver the Henry's constants (H_i , H_k) allow one to calculate – approximately – the selectivity (S_{ik}). If $S_{ik} > 10$ the sorbent in question can practically be used to purify a gas mixture (i, k) from component (i) by adsorption equilibria effects. However, it should be noted that often kinetic effects are also important in industrial adsorption processes. Hence, appropriate experiments and measurements of kinetic parameters, cp. Eq. (7.14) and Fig. 7.5, should be performed prior to a final decision on the sorbent to be chosen for the adsorption separation process in question [7.2].

The physical assumptions on which the LAI is based often hold for chemisorption processes [7.21]. For physisorption processes of gases they normally hold at low pressures and/or low coverages of the surface ($(m/m_\infty) < 0,5$) only. The term “low pressure” can be specified as

$$\begin{aligned} p &< p_s(T) & \dots T < T_c \\ p < p_R = p_c + (\partial p / \partial T)_c (T - T_c) & \dots T > T_c \end{aligned} \quad 7.23$$

Here the index (c) indicates “critical state” of the sorptive gas. The pressure (p_R) is known as Riedel pressure, an equivalent for the saturation pressure for supercritical temperatures of the gas [7.17]

The LAI often successfully has been applied to describe physisorption of supercritical gases including small non-polar molecules like (He, Ar, H_2 , N_2 , O_2 , CH_4) with small heats of adsorption ($|\Delta h| < 30 \text{ kJ/mol}$) on energetically nearly homogenous sorbent materials. Examples for these are graphitized carbon black [7.5], highly activated carbons (NORIT R1) and also porous polymers (POLYSORB, Sweden). More detailed information is provided in the extensive literature which is available today [7.1, 7.5, 7.21, 7.22].

2.1.2 Heterogeneous Surfaces

As the classical LAI only holds for energetically homogenous surfaces, but most technical sorbent materials are energetically inhomogeneous, as early as 1930 work began to extend the LAI to heterogeneous porous sorbents [7.1, 7.3, 7.5, 7.6, 7.7, 7.22]. A simple way to do this is sketched in Figure 7.6. The sorbent is assumed to consist of two types of pores: macropores offering “primary adsorption sites” (p) to gas molecules, and micropores which cannot directly adsorb molecules from the gas phase but are filled by diffusion processes of primary adsorbed molecules reaching eventually the open end of such a pore and there are adsorbed on “secondary sites” (q).

The adsorption isotherm referring to this situation is

$$\begin{aligned}
 m(p, T, m^s) &= m^p(p, T, m^s) + m^q(p, T, m^s) \\
 &= m_\infty^p(T, m^s) \frac{b^p(T)p}{1 + b^p(T)p} + m_\infty^q(T, m^s) \frac{b^q(T)p}{1 + b^q(T)p}
 \end{aligned}
 \tag{7.24}$$

It can be derived from statistical arguments similar to those leading to the classical LAI, Eq. (7.1), [7.23, 7.24].

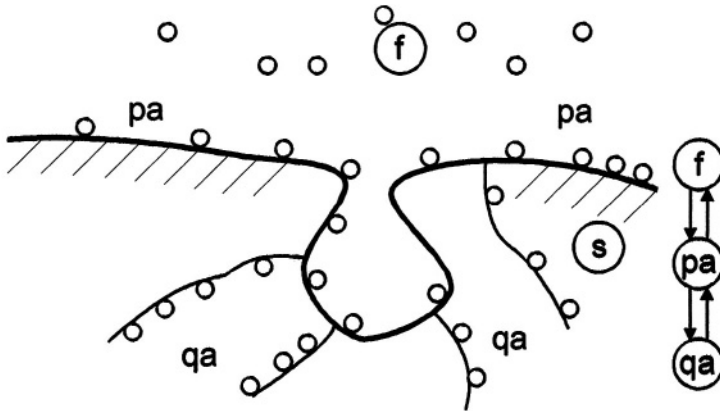


Figure 7.6. Sorbent material with two types of adsorption sites: macropores bearing primary, i. e. from the sorptive gas phase directly adsorbed molecules (pa), and micropores including secondary adsorbed molecules (qa) coming from the primary adsorbate (pa) by diffusion of the molecules.

Parameters:

- $m = Mn$... mass of adsorbate
- m^s ...mass of sorbent material
- $m_\infty^r = \lim_{p \rightarrow \infty} m^r$...limiting value of mass adsorbed for $p \rightarrow \infty$ on adsorption site of type (r = p, q). Also mass of a monolayer adsorbate of type (r).
- $b^r(T) = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} \exp\left(\frac{q^r}{RT}\right)$...Langmuir parameter for adsorption sites of type (r = p, q).
- $q^r, r = p, q$...specific heat of desorption from adsorption site of type (r).
- $R = R/M$...specific gas constant.

Enthalpy of adsorption:

$$\Delta H = H^a - H^f = -(q^p m^p + q^a m^a) < 0 \tag{7.25}$$

As an example for the AI (7.24) data of nitrogen (N₂, 5.0) adsorption on activated carbon Norit ACR1 have been correlated. Results are sketched in Figure 7.7, [7.24]. The curves refer to the primary adsorption and the total adsorption i. e. the sum of the primary and the secondary adsorbed molecules. Compared to the classical LAI the dispersion between measured and correlated data is reduced by use of the AI (7.24) by one order of magnitude. The basic idea of energetic heterogeneity presented in Fig. 7.6 easily can be extended to multi- or polyheterogeneous sorbent materials. Indeed, assuming the sorbent to include (z) many different types of adsorption sites with specific adsorption energies (-q^w, w = 1 ... z), one can derive by simple statistical arguments an adsorption isotherm of the type

$$m(p, T, m^s) = \sum_{w=1}^z m^w(p, T, m^s) \tag{7.26}$$

$$= \sum_{w=1}^z m^w(T, m^s) \frac{b^w(T)p}{1 + b^w(T)p}$$

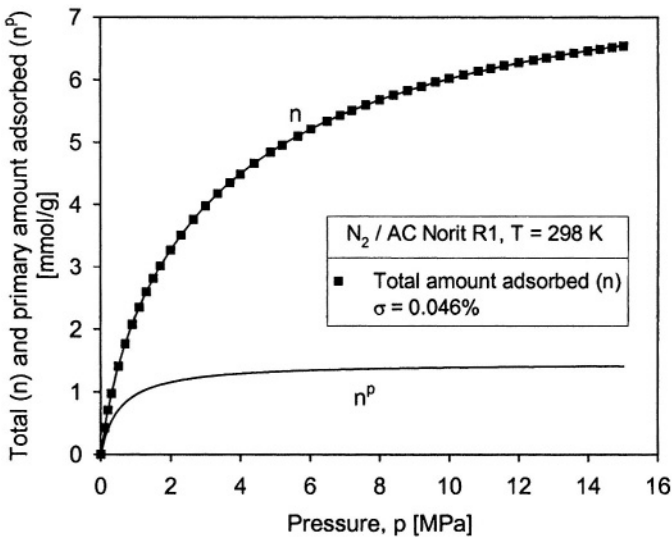


Figure 7.7. Adsorption isotherm of nitrogen (N₂, 5.0) on Norit R1 at T = 298 K. Data have been correlated by Eq. (7.24). The partial amount of N₂ adsorbed on primary sites (n^p = m^p/M_{N₂}) is presented by the lower curve. The upper curve indicates the total amount adsorbed (n = (n^p + n^a)), [7.24].

The parameters in the AI (7.26) ($m_\infty^w, b^w, w = 1 \dots z$) have the same meaning as indicated after the AI (7.24). The enthalpy of adsorption is similarly to (7.25)

$$\Delta H = H^a - H^f = - \sum_{w=1}^z q^w m^w < 0 \quad 7.27$$

The total mass which can be adsorbed for $p \rightarrow \infty$ is

$$m_\infty(T, m^s) = \sum_{w=1}^z m_\infty^w(T, m^s) \quad 7.28$$

It is interesting to consider the limit ($z \rightarrow \infty$) of the AI (7.26). Introducing the (integral distribution of the) pore spectrum $V = V(r, T, m^s)$ of the sorbent by the relation

$$dm_\infty(r, T, m^s) = \rho^L(T) dV(r, T, m^s), \quad 7.29$$

we get from Eq. (7.26) the isotherm

$$m(p, T, m^s) = \rho^L(T) \int_{r=0}^{\infty} \frac{b(r, T)p}{1 + b(r, T)p} \left(\frac{\partial V(r, T, m^s)}{\partial r} \right) dr \quad 7.30$$

In (7.29, 7.30) $\rho^L(T)$ is for $T < T_c$ the density of the sorptive medium in the liquid boiling state or, for $T > T_c$, the Riedel density $\rho^L(T) = \rho_c + (\partial \rho / \partial T)_c (T - T_c)$, the index "c" always indicating the thermodynamic critical state of the medium. For small pressures ($p \rightarrow 0$) (7.30) reduces to:

$$m(p, T, m^s) = H(T, m^s)p \quad 7.31$$

with the Henry constant given by

$$H(T, m^s) = \rho^L(T) \int_0^{\infty} b(r, T) \left(\frac{\partial V(r, T, m^s)}{\partial r} \right) dr \quad 7.32$$

The enthalpy of adsorption is

$$\Delta H = H^a - H^f = -\rho^L(T) \int_0^\infty q(r, T) \frac{b(r, T)p}{1 + b(r, T)p} \left(\frac{\partial V(r, T, m^s)}{\partial r} \right) dr \quad 7.33$$

Isotherms of type (7.30) have proved to be useful to describe adsorption of small test molecules (He, Ar, N₂) on impregnated activated carbons, the (often organic acid) impregnation providing a means to change the pore spectrum of the carbon in a prescribed way thus providing specified adsorption sites for biochemical and / or pharmaceutical molecules [7.25].

The adsorption isotherms (7.24, 7.26, 7.30) easily can be generalized to multi-component adsorption equilibria. In view of space limitations and lack of elucidating technical examples we here restrict the discussion to a mention of the coadsorption isotherm corresponding to the dual site isotherm (7.24) only, cp. also Sect. 2.1.1. The mass of component (i) adsorbed on a two site adsorbent is given by

$$\begin{aligned} m_i(p_1 \dots p_N, T, m^s) &= m_i^p(p_1 \dots p_N, T, m^s) + m_i^q(p_1 \dots p_N, T, m^s) \\ &= m_{i\infty}^p(T, m^s) \frac{b_i^p(T)p_i}{1 + \sum_{k=1}^N b_k^p(T)p_k} \\ &\quad + m_{i\infty}^q(T, m^s) \frac{b_i^q(T)p_i}{1 + \sum_{k=1}^N b_k^q(T)p_k} \end{aligned} \quad 7.34$$

Parameters:

$p_i, i = 1 \dots N$... partial pressure of component (i) in the sorptive gas mixture

$m_{i\infty}^r(T, m^s), r = p, q$... limiting loading of pure component $i = 1 \dots N$ on the adsorption sites of type ($r = p, q$).

$b_i^r(T) = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} e^{\frac{q_i^r}{R_i T}}$... Langmuir parameter of component (i) on adsorption sites of type ($r = p, q$).

$q_i^r, r = p, q$... specific heat of desorption from adsorption sites of type (r).

$q_i^r, i = 1 \dots N$... specific heat of desorption of pure component (i) from adsorption sites of type (r).

$R = R/M_i$... specific gas constant of component (i) with mole mass (M_i).

The adsorption enthalpy corresponding to (7.34) is

$$\Delta H = H^a - H^f = -\sum_{i=1}^N (q_i^p m_i^p + q_i^q m_i^q) \quad 7.35$$

Coadsorption isotherms of type (7.34) have proved to be useful for the correlations of binary and ternary coadsorption data of natural gas mixtures (CH_4 , N_2 , CO_2 , CO , H_2) on activated carbons. Details are given in [7.26].

2.1.3 Admolecules with Interactions

Admolecules often are not completely isolated from each other as indicated in Fig. 7.1, but are interacting, especially at higher surface coverages or adsorption loadings [7.6, 7.7]. Hence there have been several attempts in the literature to take these interactions into account, i. e. to extend the classical LAI to interacting admolecules on both homogeneous and heterogeneous sorbent surfaces. We here mention only the early and fundamental work of Fowler and Guggenheim (1939) [7.27], which however was not very successful in practical applications, and the work of Rudzinski & Everett (1992) [7.22], which unfortunately is very complex and not easily applicable to engineering systems and processes.

Based on a simple statistical model the classical LAI can be generalized to situations where interactions between adsorbed molecules (admolecules) on neighboring sites no longer can be neglected but explicitly have to be taken into account [7.28]. This is done by introducing the concept of “neighborhood” of admolecules in the statistical derivation of the LAI and specifying it by a simple phenomenological model. The resulting isotherm can be either of Type I, IV, or V (IUPAC) depending on numerical values of the interaction parameters. The energetic situation of the admolecules with interactions is sketched in Figure 7.8. The adsorption enthalpy consists of two parts, namely that for adsorption of an isolated admolecule (q^a) and another part reflecting the interaction between the admolecules (q^{ai}) as it occurs in densely packed micropores and – in principal – also in meso- and macropores.

$$\Delta H = H^a - H^f = -(q^a + q^{ai})m < 0 \quad 7.36$$

At low coverages approximate values are: $q^a \cong 2.5 r$, $q^{ai} \cong r$ with (r) being the heat of evaporation of the sorptive medium.

The resulting adsorption isotherm is [7.28]:

$$\theta \equiv \frac{m}{m_{\infty}} = \frac{F(\theta)p^{\alpha}}{1 + F(\theta)p^{\alpha}} \quad 7.37$$

$$F(\theta, p) = \frac{b^{\alpha} + c(1-\theta)^k}{1 + d\theta^k}, \quad k > 0 \quad 7.38$$

with

$$\lim_{p \rightarrow \infty} m = m_{\infty} \quad 7.39$$

being the limiting monolayer mass adsorbed at high gas pressures.

For small pressures ($p \rightarrow 0$) we have

$$\begin{aligned} \theta &= F(0)p^{\alpha} = (bp)^{\alpha} \\ m &= m_{\infty}(bp)^{\alpha} \end{aligned} \quad 7.40$$

Relations (7.37, 7.38) provide an implicit equation to calculate the mass adsorbed (m) from given values of the parameters ($b, c, d, k, \alpha, m_{\infty}$) and sorptive gas pressure (p). Resulting curves can be of IUPAC Type I, IV, V depending on numerical values of parameters $b > 0, c \geq 0, d \geq 0, k > 0, \alpha > 0$. Here c, d describe admolecular interactions, b is the Langmuir parameter (7.2) and k, α describe the topology of the “neighborhood” of the admolecule. Hence these parameters are related to the pore structure of the sorbent material.

As an example 3 sets of experimental data [7.29] referring to adsorption equilibria of H_2S, CO_2 and C_3H_8 on mordenite (H) at $T = 303$ for pressures up to 0.2 MPa have been correlated with both the generalized LAI (7.37, 7.38) and the simple LAI, i. e. neglecting admolecular interactions and assuming in (7.38) $a = c = 0$, but $\alpha \neq 1$. Results are presented graphically in Figures 7.9, 7.10. As can be seen, neglecting interactions between admolecules leads to systematic deviations between measured and simply correlated data, especially at higher pressures, i. e. adsorption loadings, Fig. 7.9. Correlation of data however is possible by qualitatively taking the interaction of admolecules into account, i. e. by correlating the experimental data by (7.37, 7.38), Fig. 7.10.

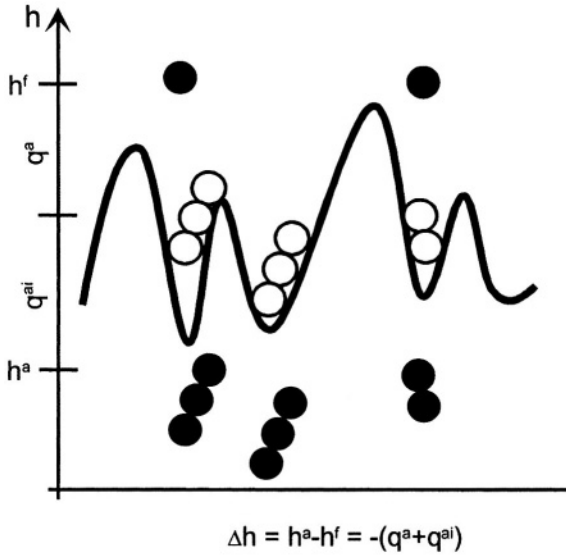


Figure 7.8. Energetic scheme of a Langmuir adsorbate with admolecular interactions. At low coverages the adsorption energy ($q^a \cong 2.5 r$) is much larger than the interaction energy of the admolecules ($q^{ai} \cong r$) with (r) being the heat of evaporation of the sorptive medium.

To elucidate this difference we mention the mean square deviation (σ) between measured (exp) and correlated (cal) data for both AIS:

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^N \left(\frac{n_{ical} - n_{iexp}}{n_{iexp}} \right)^2$$

Numerical values of (σ) in (%) are given in the scheme below:

Dispersions ($\sigma/\%$) of data correlations of adsorption equilibria of H_2S , CO_2 , C_3H_8 on microporous mordenite (H) at $T = 303$ K for pressures up to 0.2 MPa.

	H_2S	CO_2	C_3H_8
Generalized LAI (7.37)	0.25	0.40	0.75
Classical LAI ($\alpha \neq 1$)	2.63	3.49	20.7

More details about the statistical derivation and range of application of the AI (7.37, 7.38) are given in the literature [7.29, 7.30]. For the sake of

completeness we finally present the generalization of the AI (7.37, 7.38) to multicomponent systems ($N \geq 1$):

$$\theta_i = \frac{m_i}{m_{i\infty}} = \frac{F_i p_i^{\alpha_i}}{1 + \sum_k^N F_k p_k^{\alpha_k}} \leq 1, \quad i = 1 \dots N \quad 7.41$$

$$F_i(\theta_1 \dots \theta_N) = \frac{b_i^{\alpha_i} + \sum_1^N c_i \theta_1^{k_1}}{1 + \sum_1^N d_i \theta_1^{k_1}}, \quad i = 1 \dots N \quad 7.42$$

Here

$$\lim_{p_i \rightarrow \infty} \theta_i = 1, \text{ or } \lim_{p_i \rightarrow \infty} m_i = m_{i\infty}, \quad 7.43$$

i. e. $m_{i\infty}$ is the monolayer limiting mass of component ($i = 1 \dots N$) to be adsorbed at high pressures. For small pressures we have similarly to (7.40)

$$p_i \rightarrow 0 \quad m_i = m_{i\infty} F_{i=0} p_i^{\alpha_i} / \left(1 + \sum_{k \neq i}^N F_{k=0} p_k^{\alpha_k} \right) \quad 7.44$$

$$F_{k=0} \equiv F_k(\theta_1 \dots \theta_{i-1}, \theta_i = 0, \theta_{i+1} \dots \theta_N), \quad i, k = 1 \dots N \quad 7.45$$

Conversely to (7.41) we also have

$$p_i^{\alpha_i} = \frac{\theta_i}{1 - \sum_1^N \theta_1} \cdot \frac{1}{F_i}, \quad i = 1 \dots N \quad 7.46$$

this relation providing an expression allowing one to calculate the partial pressure (p_i) of component (i) necessary to keep given amounts of all components ($\theta_1 \dots \theta_N$) adsorbed.

In Eq. (7.42) (b_i) is the Langmuir parameter of component ($i = 1 \dots N$), cp. (7.17). Also parameters c_i , d_i , $1 = 1 \dots N$ describe interactions between admolecules of type (1), and (α_i , k_i , $i = 1 \dots N$) are related to the surface structure, i. e. the topology of the sorbent material [7.31]. The main physical assumptions leading to the AI (7.41, 7.42) are:

- monolayer adsorbate,
- constant adsorption enthalpies ($q_i, i = 1 \dots N$),
- densely packed admolecules so that interaction energies have to be taken into account.

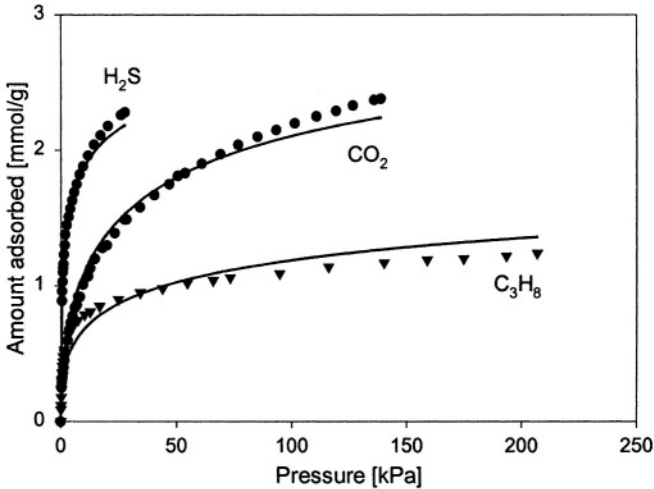


Figure 7.9. Correlation of adsorption data of H_2S , CO_2 , C_3H_8 on mordenite (H) at $T = 303$ K for pressures up to 200 kPa using the classical LAI included in (7.37, 7.38) with $\alpha \neq 1$, $a = c = 0$, [7.29, 7.24].

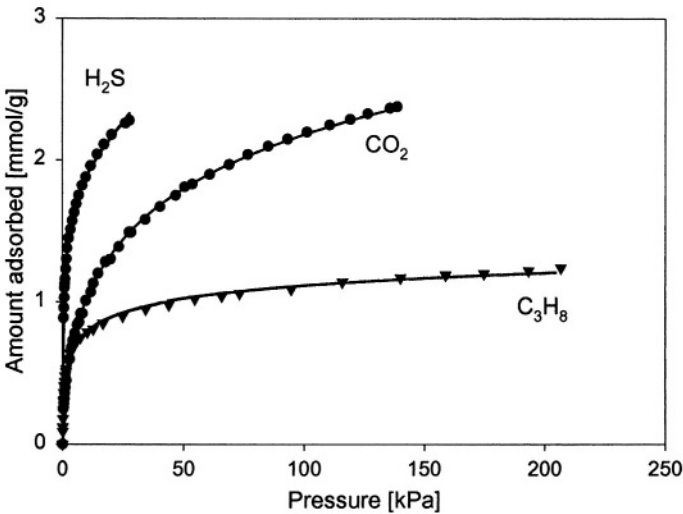


Figure 7.10. Correlation of adsorption data of H_2S , CO_2 , C_3H_8 on mordenite (H) at $T = 303$ K for pressures up to 200 kPa using the generalized LAI (7.37, 7.38) taking interactions between admolecules into account [7.28].

The coadsorption isotherms (7.41, 7.42) for $N \geq 1$ provide many implicit equations to calculate adsorption loadings $\theta_i = m_i / m_{\infty}$, $i = 1 \dots N$ if all the parameters $b_i > 0$, $c_i \leq 0$, $d_i \leq 0$, $\alpha_i > 0$, $k_i > 0$, $i = 1 \dots N$, are known. These normally have to be determined by correlating experimental coadsorption equilibria data using a Gauss minimization procedure. A detailed numerical analysis of eqs. (7.41, 7.42) is still lacking. Hence it is left as a challenge to young research students.

3. EMPIRICAL ISOTHERMS

Several of the often used empirical adsorption isotherms (AIs) are presented for single- and multicomponent systems. Hints to possible physical interpretation of parameters are given. Examples of systems to which the isotherms successfully may be applied are mentioned. Many more empirical AIs referring to anorganic, organic, and biological sorbent materials respectively can be found in the literature, cp. for example [7.3, 7.26, 7.32, 7.33]. The isotherms discussed here in brief are:

1. Freundlich-Ostwald-Boedecker
2. Virial Expansions^{*)}
3. Toth
4. Brunauer-Emmett-Teller (BET)
5. Dubinin-Polanyi
6. Integral Equation Approach

3.1 Freundlich-Ostwald-Boedecker (FOB)

Today this AI most often is known as „Freundlich-isotherm“ although it is due to the three authors mentioned [7.34]. It is a truncated Taylor-series expansion of the mass adsorbed (m) in powers of an often non-integer power ($\alpha > 0$) of the sorptive gas pressure (p):

Pure gas adsorption systems ($N = 1$):

$$m = F_1(bp)^\alpha + F_2(bp)^{2\alpha} + \dots \quad 7.50$$

^{*)} These expansions are not purely empirical but can be derived within the framework of statistical mechanics [7.43, 7.74].

Parameters:

$F_i = F_i(m^s, T)$, $i = 1, 2, 3 \dots$ Taylor-coefficients

$$b(T) = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} \exp\left(\frac{q}{RT}\right) \dots \text{Langmuir parameter, cp. (7.3).}$$

In the low pressure region, i. e. for $p \ll p_s(T)$ we have

$$p \rightarrow 0 \quad m = F_i(bp)^\alpha \tag{7.51}$$

Henry coefficient:

$$H \equiv \left(\frac{\partial m}{\partial p}\right)_{0,T} = \alpha F_i(bp)^{\alpha-1} = \begin{cases} 0 & \dots \alpha > 1 \\ F_i b \dots \alpha = 1 \\ \infty & \dots \alpha < 1 \end{cases} \tag{7.52}$$

The limiting cases $H = 0$ and $H \rightarrow \infty$ are realized – for example – for water vapor adsorption on activated carbon (AC) and hydrophilic zeolites respectively.

Multicomponent systems ($N > 1$):

$$m_i = \sum_{k=1}^N F_{ik}(b_k p_k)^{\alpha_k} + \sum_{k,l=1}^N F_{ikl}(b_k p_k)^{\alpha_k} (b_l p_l)^{\alpha_l} + \dots \quad i = 1 \dots N \tag{7.53}$$

$$p_i \rightarrow 0: m_i = \sum_{k \neq i}^N F_{ik}(b_k p_k)^{\alpha_k} + \sum_{\substack{k \neq i \\ l \neq i}}^N F_{ikl}(b_k p_k)^{\alpha_k} (b_l p_l)^{\alpha_l} + \dots, \tag{7.54}$$

$$i = 1 \dots N, \quad p_{k=\text{const}}, k \neq i$$

Parameters:

$F_{ik} = F_{ik}(m^s, T)$, $F_{ikl}(m^s, T)$... Taylor-coefficients

$$b_i = \frac{1}{p_{0i}} \sqrt{\frac{T_{0i}}{T}} \exp\left(\frac{q_i}{R_i T}\right) \dots \text{Langmuir parameter, cp. (7.17).}$$

The exponents (α_i , $i = 1 \dots N$) are related to energetic inhomogeneities and also to the fractal nature of the surface of the sorbent material [7.15, 7.35-7.37]. Numerical values are often in the range $0.2 < \alpha_i \leq 1$.

3.2 Virial Expansions

Certain functions of the number of moles (n) adsorbed on the sorbent mass (m^s) at sorptive gas pressure (p) and temperature (T) are considered as series expansions of either n or p , [7.2, 7.24, 7.38]:

$$\ln\left(\frac{n}{n_0 bp}\right) = \begin{cases} B(m^s, T)n + C(m^s, T)n^2 + \dots \\ B'(m^s, T)p + C'(m^s, T)p^2 + \dots \end{cases} \quad 7.55$$

Parameters:

- n_0 ... reference loading of a monolayer adsorbate
 $b = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} \exp\left(\frac{q}{RT}\right)$... Langmuir parameter, cp. (7.3).
 $B, B', C, C' \dots$... Virial coefficients of the adsorption system.

Equations (7.55) are also used as

$$n = n_0 bp \begin{cases} \exp(Bn + Cn^2 + \dots) \\ \exp(B'p + C'p^2 + \dots) \end{cases} \quad 7.56$$

Low pressure / loading limit ($p \rightarrow 0, n \rightarrow 0$)

$$n = n_0 bp \begin{cases} 1 + Bn + \dots \\ 1 + B'p + \dots \end{cases} \quad 7.57$$

Henry coefficient

$$H = \left(\frac{\partial n}{\partial p}\right)_{0,T} = bn_0 \quad 7.58$$

The series expansions (7.55, 7.56) are useful if Henry coefficients have to be determined from high pressure adsorption data by extrapolation to the limit ($p \rightarrow 0$). This may be necessary as low pressure adsorption measurements often are tedious, cumbersome and time consuming. Virial expansions also are used in developing microscopic models for adsorption equilibria on heterogeneous surfaces [7.38].

Multicomponent systems ($N > 1$):

$$\ln \left(\frac{n_i}{n_{i0} b_i p_i} \right) = \begin{cases} \sum_{k=1}^N B_{ik} (m^s, T) n_k + \sum_{k,l=1}^N C_{ikl} (m^s, T) n_k n_l + \dots \\ \sum_{k=1}^N B'_{ik} (m^s, T) p_k + \sum_{k=1}^N C'_{ikl} (m^s, T) p_k p_l + \dots \end{cases} \quad 7.59$$

$i = 1 \dots N$

Parameters:

$p_i = y_i p$... partial pressure of component (i) in the sorptive gas mixture

n_{i0} ... reference loading of component (i)

$b_i = \frac{1}{p_{0i}} \sqrt{\frac{T}{T_0}} \exp \left(\frac{q_i}{R_i T} \right)$... Langmuir parameter, cp. (7.17).

$B_k, B'_k, C_{kl}, C'_{kl}$... Virial coefficients of the coadsorption system.
 $k, l = 1 \dots N$

Low pressure limit of (7.59):

$$p_i \rightarrow 0, p_k = \text{const}, k = 1 \dots i-1, i+1 \dots N$$

$$n_i = n_{i0} b_i p_i \exp \left\{ \sum_{k \neq i}^N B'_{ik} p_k + \sum_{k,l \neq i}^N C'_{ikl} p_k p_l + \dots \right\} \quad 7.60$$

Henry coefficient of component (i) in the coadsorbate:

$$H_i = n_{i0} b_i \exp \left\{ \sum_{k \neq i}^N B'_{ik} p_k + \dots \right\}, \quad i = 1 \dots N \quad 7.61$$

The exponential function in this expression mirrors the influence of the other components ($k \neq i$) on the adsorption of component (i). The series expansions (7.55, 7.59) can be derived from equivalent virial expansions of the thermal equation of state (EOS) of the single- or multicomponent adsorbate by standard thermodynamic methods. Details are given in [7.2, 7.3]. Real gas effects of the sorptive gas mixture can be taken into account by replacing the partial pressures (p_i , $i = 1 \dots N$) in (7.60) by the (mixture) fugacities ($f_i = f_i(p_1 \dots p_N, T)$) of the system [7.17].

3.3 Toth's Isotherm

In 1971 J. Toth [7.39] proposed a generalization of the classical Langmuir isotherm (7.1) as

$$\begin{aligned}
 (\theta)^t &\equiv \left(\frac{n}{n_\infty} \right)^t = \frac{(bp)^t}{1 + (bp)^t} & 7.62 \\
 &= (bp)^t (1 - (bp)^t + (bp)^{2t} - \dots)
 \end{aligned}$$

Parameters:

$$n_\infty = \lim_{p \rightarrow \infty} n \quad \dots \text{ limiting amount of gas adsorbed at } T = \text{const for } p \rightarrow \infty.$$

$$\theta = \frac{n}{n_\infty} \leq 1 \quad \dots \text{ fractional loading adsorbed.}$$

$$b = \frac{1}{p_0} \sqrt{\frac{T_0}{T}} \exp\left(\frac{q}{RT}\right) \dots \text{ Langmuir parameter.}$$

$$b^{-1} = p(T, n = n_\infty / 2, m^s) \dots \text{ half-loading pressure}$$

$$0 \leq t \leq 1 \quad \dots \text{ Toth parameter describing approximately energetic heterogeneity and fractality of the surface of the sorbent.}$$

Low pressure limit and Henry coefficient

$$p \rightarrow 0 \quad \begin{aligned} n &= n_\infty bp & 7.63 \\ H &= bn_\infty & 7.64 \end{aligned}$$

The isotherm (7.62) was originally derived from the Langmuir AI (7.1) which can be written as

$$\delta \equiv \frac{\theta}{p} \left(\frac{dp}{d\theta} \right)_T = 1 + bp \quad 7.65$$

which gives a linear relation in the (δ, p) -plane. To make up for deviations of experimental δ -data from this straight line, which were caused by heterogeneities of the sorbent materials analyzed, Toth proposed instead of (7.65) the relation

$$\frac{\theta}{p} \left(\frac{dp}{d\theta} \right)_T = 1 + (bp)^t, \quad 0 < t \leq 1 \quad 7.66$$

which after integration leads to (7.62).

Multicomponent systems ($N > 1$):

$$\theta_i^t \equiv \left(\frac{n_i}{n_{i\infty}} \right)^t = \frac{(b_i p_i)^t}{1 + \sum_{k=1}^N (b_k p_k)^t}, \quad i = 1 \dots N \quad 7.67$$

p_i ... partial pressure of component i in the sorptive gas mixture.

In the low pressure limit ($p_i \rightarrow 0$, $p_k = \text{const}$, $k \neq i$), (7.67) leads to the Henry coefficient of component (i) in the coadsorbate

$$H_i = \frac{b_i n_{i\infty}}{\left(1 + \sum_{k \neq i}^N (b_k p_k)^t \right)^{1/t}}, \quad i = 1 \dots N. \quad 7.68$$

In this expression the denominator on the r.h.s. describes the impact of the other components ($k \neq i$) on the adsorption of component i in the low pressure region ($p_i \rightarrow 0$).

Today Toth's AI (7.62) is quite often used to describe adsorption of a variety of gases and vapors of organic compounds on zeolites and other inorganic sorbent materials [7.3, 7.33, 7.40-7.42].

3.4 Brunauer-Emmett-Teller Isotherm (BET)

Extending the classical Langmuir adsorption isotherm (7.1) from monolayer to ideal multilayer adsorption and considering the limiting case of infinite many layers, Brunauer, Emmett, and Teller derived in 1938 the AI [7.1-7.5, 7.42]

$$\frac{n}{n_1} = \frac{Cp/p_s}{(1 - p/p_s)(1 + (C-1)p/p_s)} \quad 7.70$$

which has IUPAC-Type II character [7.5]. Its linear form in (p) is

$$\frac{p}{n(p_s - p)} = \frac{1}{Cn_1} + \frac{C-1}{Cn_1} \cdot \frac{p}{p_s} \quad 7.71$$

Parameters:

- n ... Amount of gas adsorbed on sorbent of mass (m^s) at temperature ($T < T_C$) and (subcritical) pressure (p).
- $n_1 = n_1(T, m^s)$... amount of monolayer adsorbed on sorbent mass (m^s).
- C ... BET-parameter. It can be related to the monolayer gas pressure (p_1) and also to the inflection point of the AI (7.70) in the ($n, p/p_s$)-diagram. Statistical interpretations are given in [7.38].
- $p_s = p_s(T)$... saturation pressure of adsorptive gas.

Gas pressure (p_1) necessary for a monolayer adsorbate ($n = n_1$):

$$\left(\frac{p}{p_s} \right)_{n_1} = \frac{p_1}{p_s} = \frac{1}{1 + \sqrt{C}} \quad 7.72$$

BET-parameter:

$$C = \left(\frac{p_s}{p_1} - 1 \right)^2 \quad 7.73$$

Inflection point of the BET-isotherm [7.3]

$$C > 2: \quad \frac{p_{\text{inf}}}{p_s} = \frac{\gamma - 1}{\gamma(\sqrt{\gamma} + 1)} \quad 7.74$$

$$\gamma \equiv (C - 1)^{2/3}$$

BET-parameter

$$C = 1 + \gamma^{3/2}, \quad \gamma = \lim_{n \rightarrow \infty} \gamma_n, \quad \gamma_{n+1} = \frac{\gamma_n - 1}{(\sqrt{\gamma_n} + 1)(p_{\text{inf}}/p_s)} \quad 7.75$$

The energetic situation of the admolecules in a BET-adsorbate is sketched in Figure 7.11. A graphical representation of the BET-AI, Eq. (7.70) is given in Figure 7.12.

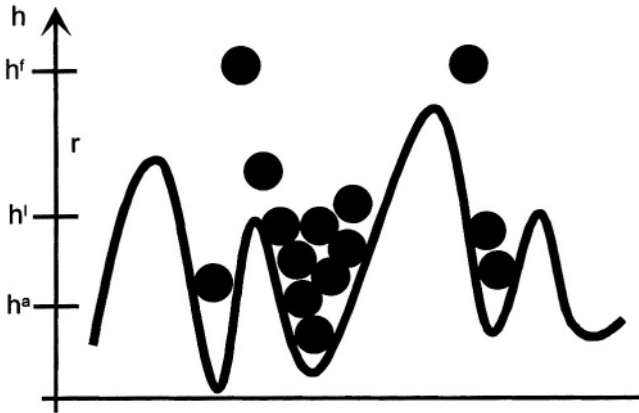


Figure 7.11. Energetic scheme of a BET adsorbate. Adsorption sites can take not only one but several molecules. Interactions between admolecules are not taken into account [7.1-7.5].

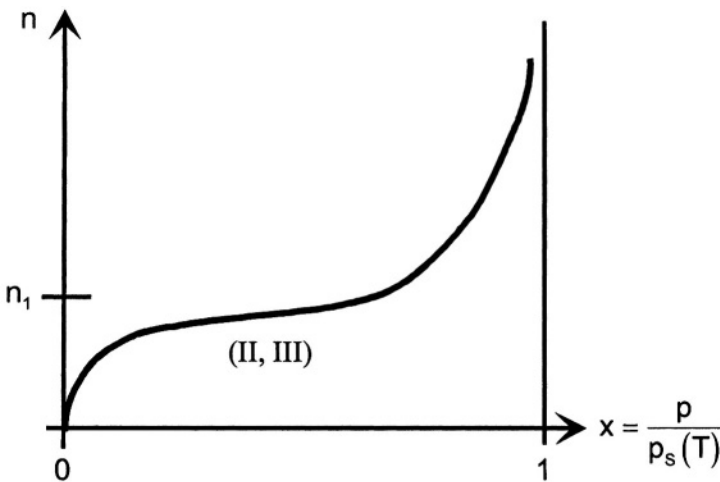


Figure 7.12. The BET-adsorption isotherm (BET AI), Eq. (7.70) showing for $C > 2$ an inflection point and at the sorptive gas saturation pressure $p = p_s(T)$ a singularity $n \rightarrow \infty$ indicating pore condensation and the appearance of a bulk liquid phase [7.1-7.5].

The BET-isotherm has been derived by statistical mechanical methods by Hill and later again by W. Steele (1974) [7.5], [7.43]. It can be shown that the infinitive number of adsorbate layers assumption used in deriving (7.70), is a reasonable approximation for multilayer adsorbates with more than 4 layers. Though admolecular interactions are not explicitly taken into account in (7.70), today this isotherm provides the basis for a standardized method to determine the mesoporous surface of porous sorbent materials by N_2 -adsorption at $T = 77$ K or Ar-adsorption at $T = 87$ K, i. e. $p_s = 0.1$ MPa. For this normally only the initial portion of a measured isotherm ($0 < p/p_s \leq 0.35$) is used. Details are given in [7.1, 7.5, 7.44-7.47] and in the respective ISO-documents published meanwhile [7.14].

A typical example of a N_2 -isotherm measured at $T = 77$ K for BET-surface determination is shown in both the linearized ($p/(n(p_s - p)), p$)-diagram and the traditional ($n, p/p_s$)-diagram in Figures 7.13, 7.14, [7.25] below. They demonstrate two typical difficulties often related to these so-called BET-measurements: the hysteresis between the adsorption- and the desorption branch indicating existence of mesopores and – in Fig. 7.13 – the deviation from the linear plot for pressures ($p/p_s > 0.4$), which is mainly due to energetic heterogeneities of the surface of the sorbent and to admolecular interactions.

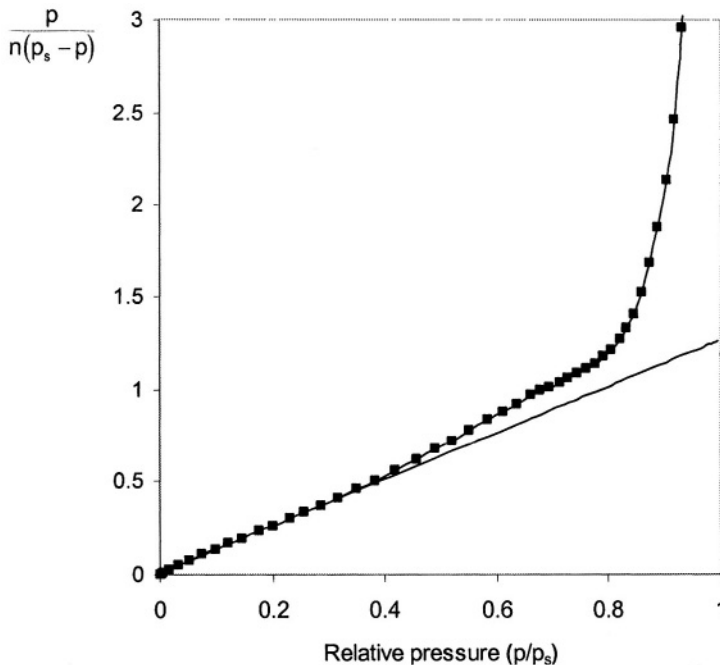


Figure 7.13. Linearized adsorption- and desorption isotherm of N_2 (5.0) on standardized material CRMBAM-PM-104 at 77 K, $p_s = 1$ atm, [7.25]. Correlation: (7.71).

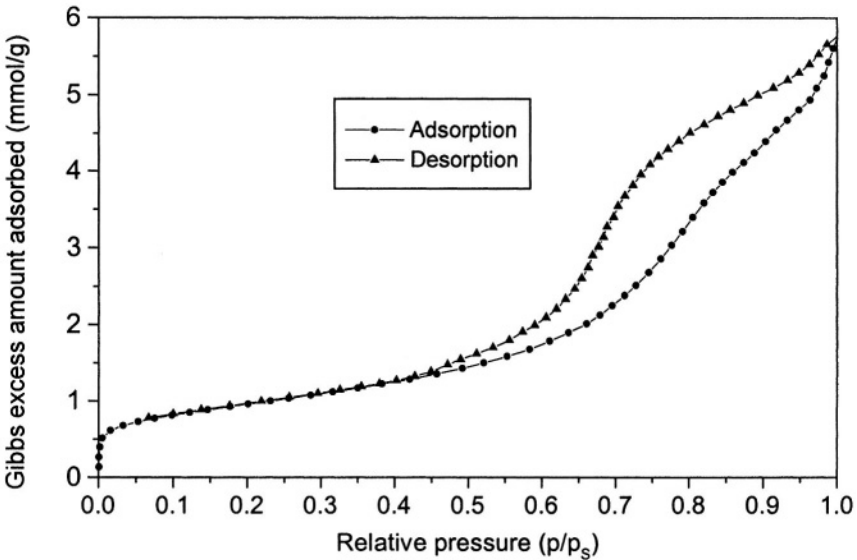


Figure 7.14. Adsorption- and desorption isotherm of N_2 (5.0) on standardized material CRMBAM-PM-104 at $T = 77$ K, $p_s = 1$ atm, [7.25].

A thermodynamic consistent extension of the BET-isotherm to multicomponent systems ($N > 1$) and to real gas adsorptives will be presented in Sect. 4 of this Chapter.

3.5 Dubinin-Polanyi Theory

Dubinin, Polanyi, and Radushkevich proposed about 1947 a simple but very useful empirical theory allowing one to calculate the amount of gas adsorbed in a microporous sorbent. The theory was based on a pore filling model. Today it is used for both characterization of porous solids and also for engineering purposes. It has been extended by several authors among them predominantly Astakhov (1970). The theory is still the subject of further investigations, mainly by statistical mechanics and computational methods (DFT) [7.1-7.3, 7.48-7.55].

The adsorbate is considered as a fluid phase in the sense of thermodynamics, cp. Sect. 7.4, which is exerted to the external forces of the atoms and molecules located on the surface of a sorbent material. The general condition for thermodynamic equilibrium of such a phase (a) against a fluid or gaseous sorptive phase (f) is [7.56, 7.57]:

$$\mu^a - \hat{\phi} = \mu^f - 0 = \text{const} \quad 7.76$$

Here μ^a , μ^f are the chemical potentials of the adsorbate and the sorptive phase and $\hat{\phi} > 0$ (for attractive forces) is the mechanical potential per unit of mass of the forces acting near the surface of the sorbent on the admolecules. Ideal gas and liquid approximations [7.17] for μ^f , μ^a lead via (7.76) to the approximate expression

$$\hat{\phi} = RT \ln \left(\frac{p_s(T)}{p} \right) \quad 7.77$$

with $p_s(T)$ indicating the saturation pressure of the sorptive mediums at temperature $T < T_c$. Assuming the portion of a micropore filled with admolecules (W) to be a function of ($\hat{\phi}$) having the form

$$W = W_0 \exp(-(\alpha \hat{\phi})^N), \quad 7.78$$

with (W_0) indicating the total volume of the pore, we get in view of (7.77):

$$W = W_0 \exp \left(- \left(\alpha RT \ln \left(\frac{p_s(T)}{p} \right) \right)^N \right) \quad 7.79$$

This is a somewhat generalized version of the so-called Dubinin-Radushkevich (RD) AI [7.48]. The mass of gas adsorbed in the pores then is

$$m = \rho_0 W \quad 7.80$$

Here ρ_0 is the density of the sorptive medium in a reference liquid state which may be chosen as the density of the saturated boiling liquid at the chosen temperature, i. e. $\rho_0 = \rho_s(T)$, [7.5, 7.3]. The parameter α in the “characteristic curve” of the sorbent material (7.78) is the reciprocal of a specific energy; the exponent N normally is limited to $2 \leq N \leq 6$ and for zeolites and activated carbons often has numerical values about $N \cong 3$. Both parameters are characteristic for a sorbent material and the micropore spectrum included in it. Details of practical applications of (7.79) and a variety of generalizations to real gas adsorptives and multicomponent systems can be found in the (still growing) literature in this field [7.53 7.55, 7.58].

3.6 Integral Equation Approach

The total mass (m) adsorbed on the surface of a porous solid of mass (m^s) can be assumed to be the integral sum of all masses (μ) adsorbed on the surfaces of pores of a certain geometrical structure (Γ), i. e. cylindrical – or slit-like etc. pores, as

$$m(p, T, m^s) = \int_{\Gamma} \mu(p, T, \Gamma) G(\Gamma, T, m^s) d\Gamma \quad 7.81$$

Here $G = G(\Gamma, T, m^s)$ is the pore distribution function of the sorbent material which due to thermal expansion / contraction of the material also (weakly) depends on the temperature (T) of the system. The function $\mu = \mu(p, T, \Gamma)$ is modelled by statistical mechanical methods, for example by the Density Functional Theory (DFT), cp. [7.44, 7.54, 7.59]. A fairly successful example for (7.81) has been developed among others by Horvath and Kawazoe (1983) [7.21, 7.44, 7.60, 7.61]. Indeed the proposed AI conversely can be used to calculate the pore distribution function $G(\Gamma, T, m^s)$ from known adsorbate masses (m) and a model function (μ) (inverse problem) [7.3, 7.21, 7.61]. Using probe molecules (He, Ar, N₂, CO₂) this method is used today to determine micro- and mesoporous distributions in sorbent materials as well [7.25, 7.44, 7.54].

We here restrict ourselves to the presentation of a fairly simple example for the AI (7.81) originally proposed by Jaroniec and Choma [7.21, 7.62]. Assuming the sorbent material to include only micropores of simple cylindrical shape of different diameters which do not interconnect, adsorption on a single pore can be described by the DR-isotherm (7.79) with $N = 2$. Assuming also the micropores to be statistically distributed according to a Γ -distribution function [7.63] of degree (n), one gets from (7.81) the isotherm

$$\frac{m(p, T, m^s)}{m_s(T, m^s)} = \left[\frac{\kappa}{\kappa + \left(\alpha RT \ln \left(\frac{p_s(T)}{p} \right) \right)} \right]^{n+1} \quad 7.82$$

Parameters:

- $m_s(T, m^s)$... mass of adsorbate in the saturation state, i. e. at completely filled pores and gas pressure $p = p_s(T)$.
 α, κ, n ... characteristic parameters of the sorbent material to

be determined from adsorption experiments with probe or yardstick molecules [7.50].

$p_s(T)$... saturation pressure of sorptive gas at $T < T_C$.
 For $T > T_C$ the so-called Riedel pressure can be used, cp. Sect. 2.1.1, (7.23).

Though the AI (7.82) has proved to be useful for characterizing microporous materials [7.62], it should always be taken into account that it refers to absolute amounts adsorbed (m) which cannot easily be measured today but in practice have to be determined approximately from Gibbs excess adsorption data, cp. Chap. 1. Hence the sorbent parameters (α , κ , n) may vary considerable depending on the type of probe molecules actually used and also the reference density of the adsorbed phase introduced, cp. Eq. (7.80).

In concluding this Section we want to emphasize that literature shows a variety of other empirical adsorption isotherms developed for special purposes and using quite different physical pictures and concepts [7.65, 7.66] and also new mathematical techniques like neural networks and/or genetic codes [7.67]. The interested reader is referred to the Proceedings of the most important Int. Conferences in the field of adsorption like COPS, FoA, PBAC, etc., cp. Chap. 1.

4. THERMODYNAMIC ISOTHERMS

4.1 Gibbs's Approach

Josiah Willard Gibbs was the first to apply thermodynamic methods to describe physisorption equilibria of gases on porous solids [7.68]. After him many other authors extended his work in several directions, especially to multicomponent systems and to its statistical mechanical foundations. Also a variety of adsorption isotherms for both single- and multicomponent systems were derived from the respective thermal equations of state for the (two-dimensional) adsorbate phase. We here mention only the classical books and papers by Young [7.69], Myers and Prausnitz [7.70], van Ness [7.71], Sircar [7.72], and Talu [7.73]. Today there are many other representations of Gibbsian adsorption thermodynamics available in literature. All of them are nearly equivalent and differ only slightly in their aims and goals. Hence, we here are not going to discuss the Gibbsian approach again but mention only some references which also are only a selection of the existing literature and in no way claim completeness: [7.2, 7.5, 7.22, 7.33, 7.40, 7.75, 7.76], [7.7,

7.53, 7.65]. The interested reader is well advised if he tries to get and read the original papers of the fathers of adsorption thermodynamics, namely J. W. Gibbs [7.74], I. Langmuir [7.64], and W. Ostwald [7.34].

4.2 Internal Variable Approach

In this Section we will present another approach to adsorption thermodynamics, the main statement being a mathematical representation theorem for adsorption isotherms of both single and multicomponent systems with real gas adsorptives on either (energetically) homogenous or inhomogeneous sorbent materials [7.15, 7.77]. From this a variety of thermodynamically consistent isotherms for multicomponent systems can easily be derived, among them generalizations of the BET- and the Aranovich-isotherms which proved to be very useful in describing coadsorption isotherms of gas mixtures including subcritical components.

Let us consider an adsorption system consisting of $N \geq 1$ many gaseous components and a chemically inert sorbent phase. In addition we have at any temperature and any set of partial gas pressures a sorbate phase which is assumed to be a thermodynamic system of fractal dimension ($1 \leq D \leq 3$) in the sense of W. Schottky and J. Meixner [7.78, 7.57, 7.56]. The parameters of the sorptive gas, the adsorbate, and the sorbent are:

Sorptive gas (f)

$p_i, \quad i=1 \dots N$... partial pressure of component i
 T ... temperature

Sorbate phase (a)

$n_i, \quad i=1 \dots N$... total amount of component i adsorbed.

This is defined experimentally by combined dielectric-calorimetric and manometric measurements, i. e. without introducing the concept of a dividing surface or that of the (accessible) volume of a porous solid, cp. Chap. 1 and [7.79].

T ... temperature,

$\pi = \gamma^s - \gamma$... spreading pressure of sorbate, i. e. the difference between the surface tensions between the (f, s)- and the (f, a, s)-phases.

Inert sorbent phase (s)

m^s ... mass

T ... temperature,

$A = A(m^s, T)$... extensive parameter of the fractal surface of the sorbent material.

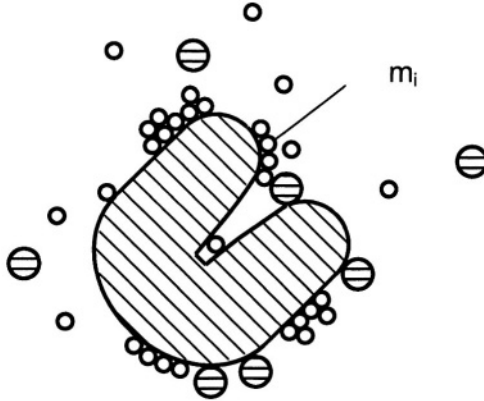


Figure 7.15. Model of an adsorption system with $N = 2$ components on the (possibly fractal) surface of an inert porous solid.

The Gibbs equation corresponding to the $(N+1)$ external operations possible on the adsorption system, namely, changing of partial pressures ($p_i, i = 1 \dots N$) and temperature (T), is [7.15, 7.17, 7.56, 7.57]

$$dG = -SdT + Ad\pi + \sum_{i=1}^N \mu_i dn_i \tag{7.90}$$

Here the spreading pressure (π) is considered as an internal variable in the sense of Bridgeman, Kestin, and Meixner [7.56, 7.57], i. e. it is not an independent variable, but a function of the external parameters $\pi = \pi(T, p_1 \dots p_N)$ of the system. From the Gibbs-Duhem-equation or, likewise, the Euler equation for $G = G(T, n_1 \dots n_N, m^s)$ being a homogeneous function of degree 1 in the mole numbers ($n_1 \dots n_N$) of the sorbate phase, we get the relations

$$A \left(\frac{\partial \pi}{\partial T} \right)_p = S + \sum_{i=1}^N \left(\frac{\partial \mu_i}{\partial T} \right)_p n_i \tag{7.91}$$

$$p_k: A \left(\frac{\partial \pi}{\partial p_k} \right)_T = \sum_{i=1}^N \left(\frac{\partial \mu_i}{\partial p_k} \right) n_i, \quad k = 1 \dots N \quad 7.92$$

These can be substituted in the total differential of the spreading pressure

$$d\pi(T, p_1 \dots p_N) = \left(\frac{\partial \pi}{\partial T} \right)_p dT + \sum_{k=1}^N \left(\frac{\partial \pi}{\partial p_k} \right)_T dp_k \quad 7.93$$

which can then be inserted into (7.90) to give

$$dG = \left(-S + A \left(\frac{\partial \pi}{\partial T} \right)_p + \sum_i^N \mu_i \left(\frac{\partial n_i}{\partial T} \right)_p \right) dT + \sum_k^N \left(A \left(\frac{\partial \pi}{\partial p_k} \right)_T + \sum_i^N \mu_i \left(\frac{\partial n_i}{\partial p_k} \right)_T \right) dp_k \quad 7.94$$

with $p = \sum_i^N p_i$ being the total gas pressure in the system. The Maxwell relation for partial pressures (p_k, p_i) is

$$\sum_i^N \frac{1}{f_i} \left(\frac{\partial f_i}{\partial p_k} \right)_T \left(\frac{\partial n_i}{\partial p_i} \right)_T = \sum_i^N \frac{1}{f_i} \left(\frac{\partial f_i}{\partial p_i} \right)_T \left(\frac{\partial n_i}{\partial p_k} \right)_T, \quad k \neq i \quad 7.95$$

$$k, i = 1 \dots N$$

Here the thermodynamic equilibria conditions

$$\mu_i = \mu_i^f, \quad i = 1 \dots N \quad 7.96$$

for the isothermal phases (a, f) have been used, μ_i^f indicating the chemical potential of component ($i = 1 \dots N$) in the sorptive phase. This quantity can be written as

$$\mu_i^f = \mu_{i0}^+(p^+, T) + RT \ln \left(\frac{f_i}{p^+} \right), \quad i = 1 \dots N \quad 7.97$$

with (μ_{i0}^+) being the chemical potential of pure component (i) at a certain reference pressure (p^+) and

$$f_i = f_i(p_1 \dots p_N, T), \quad i = 1 \dots N \quad 7.98$$

indicating the fugacity of component (i) in the gaseous mixture [7.17].

The Maxwell relations (7.95) provide a set of $N(N-1)/2$ linear partial differential equations for the adsorption isotherms

$$n_i = n_i(p_1, \dots, p_N, T, m^s), i = 1 \dots N \quad 7.99$$

A class of solutions of (7.95) is given by [7.15]^{*)}

$$n_i(p_1, \dots, p_N, T, m^s) = n_\infty(T, m^s) \left[\alpha_i c_i^{\alpha_i} + \frac{f_i}{RT} \sum_{k=1}^N \alpha_k c_k^{\alpha_k} \left(\frac{\partial q_k}{\partial f_i} \right) \right] \Phi(c^*) \quad 7.100$$

with

$$c_i = \frac{f_i}{p_{i0}} e^{\frac{q_i}{RT}}, \quad i = 1 \dots N, \quad 7.101$$

$$c^* = \sum_i^N c_i^{\alpha_i} \quad 7.102$$

and

$$q_i = q_i(f_1, \dots, f_N, T), \quad i = 1 \dots N \quad 7.103$$

being the pressure (or – equivalently – the fugacity) dependent molar adsorption energies. Assuming for the fugacities the limiting behavior

$$\lim_{p_i \rightarrow \infty} f_i(p_1 \dots p_N, T) \rightarrow \infty, \quad i = 1 \dots N \quad 7.104$$

and restricting ourselves to “characteristic functions” Φ obeying the limiting condition $\lim_{x \rightarrow \infty} (x\Phi(x)) = 1$, one can derive from (7.100) that there exist limiting loadings for $p_i \rightarrow \infty$, $p_k = \text{const}$, $k = 1 \dots i - 1, i+1 \dots N$:

*) More solutions can be found provided one can spend a sabbatical term in a stimulating environment being far away from any kind of administration.

$$\lim_{p_i \rightarrow \infty} n_i = \alpha_i n_\infty, \quad i = 1 \dots N \tag{7.105}$$

For spherical or nearly spherical molecules the exponents ($\alpha_i > 0$) are related to their molecular radii as

$$\frac{\alpha_i}{\alpha_0} = \left(\frac{r_i}{r_0} \right)^{-D}, \quad i = 1 \dots N \tag{7.106}$$

Here (D) is the fractal dimension of the surface of the sorbent material [7.35-7.37, 7.5, p. 183]. The index “0” refers to a reference molecule, which on principle can be chosen arbitrarily. In practice Argon has turned out to be the most useful probe sorptive gas.

As an example some sets of (α , r , D)-data which have been obtained from pure supercritical gas adsorption data are presented in Tab. 7.2 below [7.76].

AC/Z	α			$2r / \text{Å}$			D
	N_2	Ar	CH_4	N_2	Ar	CH_4	
WS IV	0.8404	0.8662	0.7758	3.7	3.65	3.81	2.7
Norit	0.8264	0.8706	0.8028	3.7	3.62	3.75	2.4
AKF	0.670	-	0.540	3.7	-	4.0	2.85
DAY	0.8293	-	0.7838	3.7	-	3.8	2.3

Table 7.2. Numerical values of exponents (α_i) and molecular radii (r_i) for adsorption of gases ($i = N_2, Ar, CH_4$) on zeolites WS IV and DAX and activated carbons Norit R1 and AKF, [7.76].

The difference of enthalpies in the sorptive gas and the sorbate state corresponding to the isotherms (7.100) can be calculated from the general relation

$$H^f - H^a = -AT \left(\frac{\partial \pi}{\partial T} \right)_p \tag{7.107}$$

and Eq. (7.91). The result is

$$H^f - H^a = \sum_i^N \left[\left(q_i - \frac{RT^2}{f_i} \left(\frac{\partial f_i}{\partial T} \right) \right) n_i - n_\infty \Phi(c^*) \frac{q_i f_i}{RT} \sum_k^N \alpha_k c_i^{\alpha_k} \left(\frac{\partial q_k}{\partial f_i} \right)_T \right] \tag{7.108}$$

The function Φ in representations (7.100), (7.107) is a so-called characteristic function of the adsorption system. It is due to several restrictions which are based on thermodynamic stability conditions, i. e. the Second Law [7.17, 7.56]:

$$\Phi = \Phi(x) \geq 0 \quad \text{all } x \geq 0 \quad 7.109$$

$$\frac{d}{dx}(x\Phi(x)) \geq 0 \quad 7.110$$

Examples of characteristic functions obeying these conditions are:

Langmuir

$$\Phi(x) = \frac{1}{1+x}, \quad 7.111$$

BET

$$\Phi(x) = \frac{C}{(1-x)1+(c-1)x}, \quad C > 0 \quad 7.112$$

Aranovich

$$\Phi(x) = \frac{D}{(1-x)^{1/2}(1+Dx)}, \quad D > 0 \quad 7.113$$

Many more functions obeying inequalities (7.109, 7.110) exist but are still subject to investigation.

Inserting the functions (7.111-7.113) into (7.100), (7.108) one gets thermodynamic consistent generalizations of the Langmuir, BET, and Aranovich AIs to adsorption systems with

- a) an arbitrary number of components ($N \geq 1$),
- b) real gas sorptive media described by their fugacities ($f_1 \dots f_N$),
- c) loading or pressure dependent adsorption energies ($q_1 \dots q_N$), cp. (7.103),
and

d) a sorbent characteristic fractal exponent (D) relating the limiting loadings of sorptive gases according to the size of their molecules, cp. Eqs. (7.105, 7.106).

As an example we here only mention the generalized form of the Langmuir AI resulting from Eqs. (7.100, 7.111) with an sorptive ideal gas mixture, i. e. $f_i = p_i$, $i = 1 \dots N$, but loading dependent adsorption energies an example of which is given by [7.15]:

$$q_i = \frac{1 + \sum_m a_m p_i}{1 + \sum_m b_m p_i} q_{i0} \quad 7.114$$

with empirical parameters (a_{im}, b_{im} , $i=1 \dots N$) and initial values $q_i(p_k = 0) = q_{i0}$, $i = 1 \dots N$).

Adsorption isotherms:

$$n_i(p_1 \dots p_N, T) = n_\infty(T) \left[\alpha_i c_i^{\alpha_i} + \frac{p_i}{RT} \sum_m \alpha_m c_m^{\alpha_m} \left(\frac{\partial q_m}{\partial p_i} \right)_T \right] \frac{1}{1 + \sum_k c_k^{\alpha_k}} \quad 7.115$$

Adsorption enthalpy:

$$H^f - H^a = \sum_i \left[q_i n_i - n_\infty \frac{p_i q_i}{\left(1 + \sum_k c_k^{\alpha_k} \right) RT} \sum_m \alpha_m c_m^{\alpha_m} \left(\frac{\partial q_m}{\partial p_i} \right)_T \right] \quad 7.116$$

with

$$c_i = \frac{p_i}{p_{i0}} e^{q_i/RT}, \quad i = 1 \dots N \quad 7.117$$

Equations (7.115) and (7.116) have very similar structures: The first terms on their r.h.s always are due to the components (i), whereas the second terms describe mixture effects mainly caused by the loading (or pressure) dependence of the adsorption energies $q_i = q_i(p_1 \dots p_N, T)$, $i = 1 \dots N$, cp.

example (7.114), i. e. these terms vanish if $q_i = \text{const}$, $i = 1 \dots N$, can be assumed.

Finally we want to emphasize that the many parameter isotherms represented in Eqs. (7.100) (and – as an example – in Eq. (7.115)) together with the respective enthalpy functions (7.108) and (7.116) only should be used if there are enough experimental adsorption data available. This means, if the number of (reliable) data points well exceeds the square of the number of parameters included in these equations. The numerical values of these parameters have to be determined by appropriate data correlation procedures, i. e. those which take uncertainties of experimental data well into account.

5. CONCLUSIONS

As has been mentioned in the Introduction to this Chapter, there is no single isotherm which can describe all physisorption phenomena occurring when pure or mixed gases contact the surface of a porous solid. This mainly is due to the complexity of the admolecule – sorbent atom/molecule interactions and, at higher loadings, also the admolecule – admolecule interaction. This complexity is a consequence of the energetic heterogeneity of the adsorption sites, the great variety of pores in shape, size, and connectivity, i. e. the pore spectrum of the sorbent, and also of the various properties of the adsorptive molecules, for example their electrical moments (dipole, quadrupole etc.) and their topography. In case of gas mixtures special mixture effects may occur in addition, for example pore blocking by the larger molecules thus preventing the smaller to enter.

Nevertheless, for practical applications very rough recommendations about adsorption isotherms to be expected in experiments or to be used in industrial processes can be given. They are summarized in Table 7.3 below where sorbent materials simply are classified according to their pore spectrum as “narrow” (zeolites, molecular sieves, etc.) or “wide” (activated carbons, silica, etc.). In the first case we mainly expect microporous sorbent materials, whereas in the second case micro-, meso-, and macropores as well can be included in the sorbent.*) The adsorptive molecules are classified by their polarity as either non-polar like (He, Ar, N₂, O₂, CH₄) or polar like (CO, NO,

*) We do not consider so-called “periodic mesoporous materials”, for example certain organosilicas, which do have a very narrow mesopore spectrum and presently are subject to intensive investigations.

H₂O, SO₂, CCl₄, F₂, H₄-i-j, etc.). For sake of simplicity, no structure or size arguments are taken into account.

For all isotherms mentioned in Table 7.3, extensions to multicomponent systems exist and have been mentioned in Sects. 2-4. However, it must be emphasized that in mixture adsorption it is often very difficult to predict or calculate the amounts of the lesser (or weakly) adsorbed components. Hence reliable measurements of coadsorption equilibria are recommended again.

Generally speaking for low gas pressures and high temperatures conditions ($p \rightarrow 0, T \rightarrow \infty$) physisorption of gas molecules decreases and isotherms are normally of either linear, i. e. Henry-type or of Freundlich-type. The linear region of the isotherm strongly depends on the nature of the sorptive gas. For H₂ at 298 K (supercritical) AIs on ACs are often linear up to 8 MPa, whereas for CO₂ at 298 K (subcritical) deviations from the linear region at about 0.5 MPa can be observed. For high pressures and high temperatures ($p \rightarrow \infty, T \rightarrow \infty$) physisorption of gas molecules increases and isotherms of Langmuir – type can be expected, cp. Sect. 2.1.1. For high pressures and low temperatures ($p \rightarrow \infty, T \rightarrow 0$) physisorption normally will lead to pore condensation and isotherms of BET- or Freundlich-type should be expected.

Table 7.3. Adsorption isotherms recommended to describe gas adsorption equilibria in sorbent materials with

- a) narrow pore spectra:
Zeolites, molecular sieves, carbon molecular sieves etc.
- b) wide pore spectra:
Activated carbons, silica, activated alumina etc.

		Sorbent Material Pore Spectrum	
		Narrow	Wide
Sorbitive Gases	f \ s	Langmuir Virial Expansion Dubinin-Polanyi	BET Integral Equation Ideal Adsorbed Solution Theory
	Nonpolar He, Ar, N ₂ O ₂ , CH ₄ CO ₂	Langmuir Freundlich et al. Toth	BET Integral Equations Toth
	Polar H ₂ O, H ₂ S SO ₂ VOCs	Zeolite, Molecular Sieve, Carbon Sieves	Activated Carbons, Silica, Act. Alumina

As far as industrial adsorption processes are concerned it always should be taken into account that isotherms which are favorable for adsorption normally are unfavorable for desorption processes. Also, for column performance, for example packed bed dynamics, the velocity of the mass break through front is inverse proportional to the steepness of the adsorption isotherm. Hence it can be decisive to have accurate equilibria data at hand to get reasonably accurate values of the respective differential quotients [7.2, 7.4, 7.40]. For mixture adsorption this argument becomes even more important. S. D. G.

6. LIST OF SYMBOLS

A	m^D	areal extension parameter of a sorbate considered as thermodynamic phase of fractal dimension ($1 \leq D \leq 3$)
$b = (p(T, m = m_\infty/2, m^s))^{-1}$	Pa^{-1}	Langmuir parameter, also reciprocal of half-loading pressure
$b_i = (p_i(T, m_i = m_{i\infty}/2, m^s))^{-1}$	Pa^{-1}	Langmuir parameter of component $i = 1 \dots N$, also reciprocal of half loading pressure of pure component (i)
$f_i(p, T)$	Pa	fugacity of component $i = 1 \dots N$ in a sorptive gas mixture, cp. Eq. (7.97)
$H = \left(\frac{\partial m}{\partial p} \right)_{0,T}$	gPa^{-1}	Henry's constant of an adsorbate in the low pressure limit ($p \rightarrow 0$)
$H_i = \left(\frac{\partial m_i}{\partial p_i} \right)_{0,T,p_k}$	gPa^{-1}	Henry's constant of component $i = 1 \dots N$ of a coadsorbate in the low pressure limit ($p_i \rightarrow 0$)
H^a	J	enthalpy of mass (m) of adsorbate
H^f	J	enthalpy of mass (m) of sorptive gas
m	kg	mass of an adsorbate on a certain mass (m^s) of sorbent
M	g/mol	molar mass of sorptive gas
m_∞	kg	limiting value of mass adsorbed on sorbent of mass (m^s) for high pressures ($p \rightarrow \infty$)